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ELECTRICAL PROPERTIES OF MATERIALS : BAND THEORY OF SOLIDS

5.1 INTRODUCTION

We know that each metal contains a large number of free electrons (conduction electrons). Drude in 1900 proposed a classical model which is known as *free electron theory*. The electrons are assumed to be completely free except for a potential at the surface so that they move about inside the metal. The conduction electrons are regarded as *free electron gas*. The theory explains successfully a number of observed facts of the solid but fails in some other cases.

The free electron theory failed to explain the difference between metals (conductors), semiconductors and insulators. The cases in which free electron theory fails, quantum mechanical concepts provide a simpler way. Actually, band concepts has been very useful to explain for solving such problems.

The failure of the free electron model is due to the oversimplified assumption that a conduction electron in a metal experiences a constant or zero potential due to the ion cores and hence is free to move about in a crystal; the motion being restrained only by the surface of the crystal. In fact, the potential due to ion cores is not constant and may change with position of the electron in the crystal. Some contribution to potential may also arise because of the other electrons present in the crystal. Thus the actual nature of potential under which an electron moves in a crystal is very complicated.

According to band theory, an electron in a crystal is that of a single electron in perfectly periodic potential which has the periodicity (a) of the lattice as shown in fig.(23.6).

23.3 PERIODIC POTENTIAL IN A CRYSTAL

The potential energy of an electron at a distance r from an atomic nucleus of charge $+Ze$ is given by

$$V = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}$$

The variation of potential energy V with distance r for an isolated system is shown in Fig. 23.5.

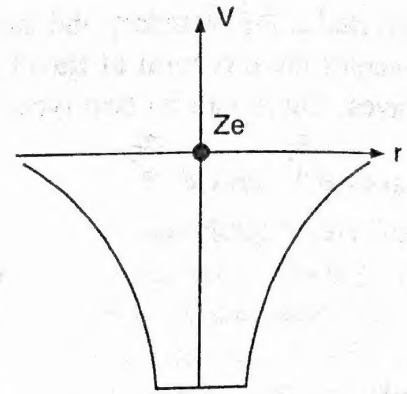


Fig. 23.5

When a crystal is formed a number of such atomic nuclei are brought close to each other. The potential of an electron in such a case is the sum of the potential energies due to individual nuclei. The variation of potential energy with distance in a *one dimensional* case is shown in Fig. 23.6.

The atomic nuclei have a positive charge and the electrostatic potential energy of an electron in the field of positive charge is *attractive, i.e., negative*. This is why the potential energy is shown along the $-V$ axis. To a reasonable approximation the nuclei (or ion cores) have been considered

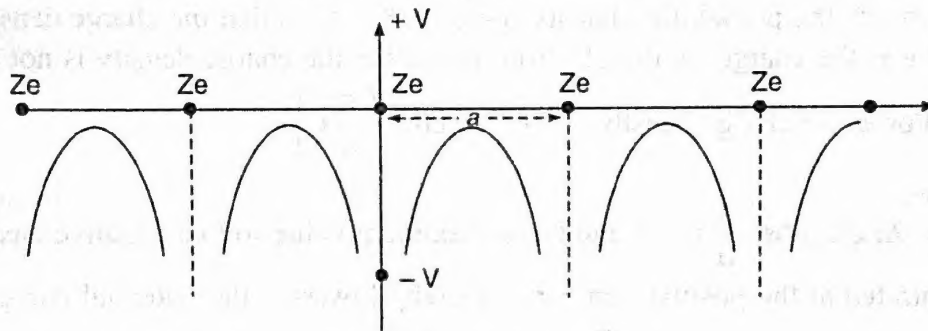


Fig. 23.6.

at rest and the potential experienced by an electron in the crystal is assumed to be periodic with the period equal to the lattice constant a . The quantity ' a ' is also known as lattice parameter.

23.4 BLOCH THEOREM

In the free electron theory, the electron is supposed to move in a constant potential V_0 and Schrodinger's wave equation for a one dimensional case is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi = 0 \quad \dots (i)$$

The solution of this equation is

$$\psi(x) = e^{\pm ikx}$$

where

$$k^2 = \frac{2m}{\hbar^2} (E - V_0)$$

\therefore

$$E - V_0 = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{4\pi^2} \cdot \frac{4\pi^2}{\lambda^2} \cdot \frac{1}{2m} = \frac{\hbar^2}{\lambda^2} \cdot \frac{1}{2m} = \frac{p^2}{2m} = E_{\text{kinetic}}$$

The physical meaning of k is that it represents the momentum of the electron divided by \hbar as shown:

The magnitude of $\vec{k} = |\vec{k}| = \frac{2\pi}{\lambda} = 2\pi \frac{mv}{h} = \frac{mv}{\hbar} = \frac{p}{\hbar}$

Each electron will have its own \vec{k} and its own energy.

For an electron moving in a one dimensional periodic potential the potential energy is given by the relation

$$V(x) = V(x + a)$$

where a is the period equal to lattice constant. In this case Schrödinger's equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi = 0 \quad \dots (ii)$$

With reference to the solution of this equation there is an important theorem known as *Bloch theorem* or *Floquet's theorem* which states that there exist solutions of the form

$$\psi(x) = e^{\pm ikx} \mu_k(x) \quad \dots (iii)$$

where

$$\mu_k(x) = \mu_k(x + a) \quad \dots (iv)$$

Thus the solutions are plane waves of the type $e^{\pm ikx}$ modulated by the function $\mu_k(x)$ which has the same periodicity as the lattice constant.

The wave function of the type $\psi(x) = e^{\pm ikx} \mu_k(x)$ is called *Bloch function*. The wave vector \vec{k} gives the direction of Bloch wave.

Proof. Suppose $f(x)$ and $g(x)$ are two real and independent solutions of equation (ii). Then the general solution is

$$\psi(x) = A f(x) + B g(x) \quad \dots (v)$$

where A and B are arbitrary constants. As the potential is periodic, i.e., $V(x) = V(x + a)$, therefore, the functions $f(x + a)$ and $g(x + a)$ must also be the solutions of equation (ii). Since a differential equation of the second order can have only two independent solutions, the functions $f(x + a)$ and $g(x + a)$ must be able to be expressed in terms of functions $f(x)$ and $g(x)$, i.e.,

$$f(x + a) = \alpha_1 f(x) + \alpha_2 g(x) \quad \dots (vi)$$

and

$$g(x + a) = \beta_1 f(x) + \beta_2 g(x) \quad \dots (vii)$$

where $\alpha_1, \alpha_2, \beta_1$ and β_2 are real functions of energy E .

According to Eq. (v), the general solution of Schrodinger's equation is

$$\psi(x) = A f(x) + B g(x)$$

and

$$\psi(x + a) = A f(x + a) + B g(x + a)$$

According to Eq. (vi) and (vii), we have

$$\begin{aligned} \psi(x + a) &= A\alpha_1 f(x) + A\alpha_2 g(x) + B\beta_1 f(x) + B\beta_2 g(x) \\ &= (A\alpha_1 + B\beta_1)f(x) + (A\alpha_2 + B\beta_2)g(x) \end{aligned} \quad \dots (viii)$$

Now select A and B such that

$$A\alpha_1 + B\beta_1 = \lambda A \quad \dots (ix)$$

and

$$A\alpha_2 + B\beta_2 = \lambda B \quad \dots (x)$$

where λ is a constant. Substituting in Eq. (viii), we get

$$\begin{aligned} \psi(x + a) &= \lambda A f(x) + \lambda B g(x) \\ &= \lambda (A f(x) + B g(x)) = \lambda \psi(x) \end{aligned} \quad \dots (xi)$$

Equations (ix) and (x) will give non-zero values of A and B if the determinant of their coefficient vanishes, i.e.,

$$\begin{vmatrix} \alpha_1 - \lambda & \beta_1 \\ \alpha_2 & \beta_2 - \lambda \end{vmatrix} = 0$$

or

$$\lambda^2 - (\alpha_1 + \beta_2)\lambda + \alpha_1\beta_2 - \alpha_2\beta_1 = 0 \quad \dots (xii)$$

We shall first prove that $\alpha_1\beta_2 - \alpha_2\beta_1 = 1$ as given below.

As $f(x)$ and $g(x)$ are two real and independent solutions of Eq. (ii), we have

$$\frac{d^2 f(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] f(x) = 0 \quad \dots (xiii)$$

and
$$\frac{d^2 g(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] g(x) = 0 \quad \dots (xiv)$$

Multiplying Eq. (xiii) by $g(x)$ and Eq. (xiv) by $f(x)$ and subtracting former from the latter, we get

$$f(x) \frac{d^2 g(x)}{dx^2} - g(x) \frac{d^2 f(x)}{dx^2} = 0$$

or
$$f(x) \frac{dg(x)}{dx} - g(x) \frac{df(x)}{dx} = \text{a constant}$$

The left hand side is called Wronskian, $W(x)$ of the solution and is constant in this case.

$$\therefore W(x) = f(x) \frac{dg(x)}{dx} - g(x) \frac{df(x)}{dx}$$

Now from Eq. (vi) and (vii), we get

$$\begin{aligned} W(x+a) &= f(x+a) \frac{dg(x+a)}{dx} - g(x+a) \frac{df(x+a)}{dx} \\ &= f(x+a) \left[\beta_1 \frac{df(x)}{dx} + \beta_2 \frac{dg(x)}{dx} \right] - g(x+a) \left[\alpha_1 \frac{df(x)}{dx} + \alpha_2 \frac{dg(x)}{dx} \right] \\ &= [\alpha_1 f(x) + \alpha_2 g(x)] \left[\beta_1 \frac{df(x)}{dx} + \beta_2 \frac{dg(x)}{dx} \right] \\ &\quad - [\beta_1 f(x) + \beta_2 g(x)] \left[\alpha_1 \frac{df(x)}{dx} + \alpha_2 \frac{dg(x)}{dx} \right] \\ &= (\alpha_1\beta_2 - \alpha_2\beta_1) \left[f(x) \frac{dg(x)}{dx} - g(x) \frac{df(x)}{dx} \right] \\ &= (\alpha_1\beta_2 - \alpha_2\beta_1) W(x) \quad \dots (xv) \end{aligned}$$

Thus, $W(x+a) = (\alpha_1\beta_2 - \alpha_2\beta_1) W(x)$

But $W(x+a) = W(x) = \text{a constant}$

$$\therefore \alpha_1\beta_2 - \alpha_2\beta_1 = 1$$

Hence, Eq. (xii) becomes

$$\lambda^2 - (\alpha_1 + \beta_2) \lambda + 1 = 0 \quad \dots (xvi)$$

The quantity $(\alpha_1 + \beta_2)$ is a real function of energy E . There are two roots λ_1 and λ_2 of this quadratic equation, so there will be two functions $\psi_1(x)$ and $\psi_2(x)$ which have the property $\psi(x+a) = \lambda\psi(x)$. The product of the two roots $\lambda_1\lambda_2 = 1$.

We consider the following cases:

(i) For energy ranges such that $(\alpha_1 + \beta_2)^2 < 4$. In such a case Eq. (xvi), will have complex roots. Since $\lambda_1\lambda_2 = 1$ these roots will be complex conjugate of each other. Therefore, we write

$$\lambda_1 = e^{ika} \quad \text{and} \quad \lambda_2 = e^{-ika}$$

where k is real.

The corresponding functions $\psi_1(x)$ and $\psi_2(x)$ will then have the property

$$\psi_1(x+a) = e^{ika} \psi_1(x) \quad \dots (xvii)$$

$$\text{and} \quad \psi_2(x+a) = e^{-ika} \psi_2(x) \quad \dots (xviii)$$

Thus in general

$$\psi(x+a) = e^{\pm ika} \psi(x) \quad \dots (xix)$$

It can be seen that a function having the property given by Eq. (xix) is the Bloch function of the type given in Eq. (iii)

$$\text{i.e.,} \quad \psi(x) = e^{\pm ikx} \mu_k(x)$$

by replacing x by $(x+a)$, then we get

$$\begin{aligned} \psi(x+a) &= e^{\pm ik(x+a)} \mu_k(x+a) \\ &= e^{\pm ika} e^{\pm ikx} \mu_k(x) \end{aligned}$$

$$\text{because} \quad \mu_k(x+a) = \mu_k(x) \quad \text{Also } e^{\pm ikx} \mu_k(x) = \psi(x)$$

$$\therefore \quad \psi(x+a) = e^{\pm ika} \psi(x) = \lambda \psi(x) \quad \dots (xx)$$

$$\text{where} \quad \lambda = e^{\pm ika}$$

We, therefore, find that Eq. (xix) and Eq. (xx) are the same. This proves Bloch theorem.

(ii) For the energy range such that $(\alpha_1 + \beta_2)^2 > 4$. In such a case Eq. (xvi) will have real roots λ_1 and λ_2 , which may be taken as

$$\lambda_1 = e^{\mu a} \quad \text{and} \quad \lambda_2 = e^{-\mu a}$$

where μ is real. The corresponding solutions to the Schrödinger's equation are

$$\psi_1(x) = e^{\mu x} \mu(x) \quad \text{and} \quad \psi_2(x) = e^{-\mu x} \mu(x) \quad \dots (xxi)$$

Though mathematically valid, these wave functions are not allowed because these functions become infinite at $+\infty$ or $-\infty$, i.e., they are not bounded functions.

The roots $\lambda_1 = e^{ika}$ and $\lambda_2 = e^{-ika}$ (allowed roots) as well as the roots $\lambda_1 = e^{\mu a}$ and $\lambda_2 = e^{-\mu a}$ (forbidden roots) are functions of $(\alpha_1 + \beta_2)$, hence of energy E . The allowed roots correspond to the *allowed energy regions* and the forbidden (or disallowed) roots are associated with *forbidden energy regions*. This means that the energy spectrum of an electron moving in a periodic potential consists of allowed and forbidden energy regions or bands.

The theory given by Bloch leading to the existence of allowed and forbidden energy regions (called bands) is supported by model suggested by Kronig and Penney. Let us study this Kronig-Penney model in detail.